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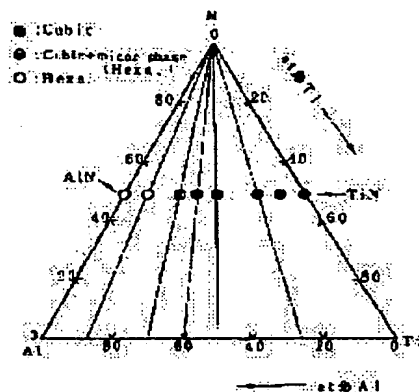
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(54) WEAR RESISTANT FILM COATED MEMBER

(57)Abstract:

PURPOSE: To produce a member in which a wear resistant film is formed with superior adhesion on the surface of a milling tool, etc., by forming an (Al, Ti) (N, C) wear resistant film having respectively specified composition and thickness on the surface of a base material.

CONSTITUTION: This wear resistant film coated member can be produced by forming a wear resistant film having a chemical composition represented by (Al_x, Ti_{1-x}) (N_y, C_{1-y}) and also having 0.8-10 μm film thickness on the surface of a base material, where $0.56 \leq x \leq 0.75$ and $0.6 \leq y \leq 1$ are satisfied. These component ranges are within the compositional range having NaCl type (B1 structure), and this film is an ALN solid solution into which TiN is allowed to enter by 25-44 mole %. When Al layer (x) exceeds the upper limit, the film composition becomes approximate to AlN, and as a result, the film is softened and sufficient hardness cannot be obtained and flank wear becomes liable to occur. On the other hand, when (x) is below the lower limit, oxidation starting temp. becomes $\leq 800^{\circ}\text{C}$. Hardness is increased and wear resistance is improved with the decrease in (y) but oxidation resistance is deteriorated and crater wear becomes liable to occur when it is below the lower limit.



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CLAIMS

[Claim(s)]

[Claim 1] On a base-material front face ($\text{Al}_x\text{Ti}_{1-x}$) (Ny C_{1-y})

however -- Wear-resistant coat covering member characterized by forming the wear-resistant coat of 0.8 to 10 micrometer thickness which consists of a chemical composition shown by $0.56 \leq x \leq 0.75$ $0.6 \leq y \leq 1$.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the wear-resistant coat covering member which comes to carry out covering formation with the adhesion excellent in the wear-resistant coat which was degree of hardness / abrasion resistance, thermal resistance,] excellent in the base-material front face in detail about the member as which the abrasion resistance which is represented with a milling tool etc. is required.

[0002]

[Description of the Prior Art] When manufacturing a high speed tool steel, cemented-carbide-tool steel, etc., forming the wear-resistant coat which becomes the front face of a tool base material from nitrides and carbide, such as Ti, is performed for the purpose of having excelled performances, such as abrasion resistance, more. As a tool by which such a demand is made, mine engineering-works tools, such as abrasion-resistant *** tools [, such as cutting-tool; chips, such as a chip, a byte, a cutter an end mill, and a drill, metal mold a die, a roll, and a shearing tool,]; or a bit, and a rod, are known.

[0003] As the technique of forming a wear-resistant coat in a base-material front face, CVD (chemical vapor deposition) and PVD (physical vapor deposition) are known conventionally. However, by the former technique, since there was a possibility that it might originate in high temperature processing and the property of a base material might deteriorate, as wear-resistant coats, such as a tool, coats, such as TiN formed by the latter technique, etc. were used widely. TiN coat demonstrates the function which thermal resistance is good and suppresses the crater of the tool rake face by the temperature increase by plastic working and frictional heat at the time of cutting.

[0004] However, in the field of recent years, for example, a cutting tool, much more improvement in the speed of a cutting speed was demanded, and for a certain reason, by the conventional wear-resistant coat which was described above, it became what cannot fully respond to this request, severe-ization of a cutting conditions advancing. Or severe-ization of a service condition is progressing [in / various machine fields other than a tool / further / tool / mine engineering-works / tool fields other than a cutting tool, for example, an abrasion-resistant *** tool,] / , and the development of the coat in which enhancement, the much more wear-resistant thermal resistance, and the much more wear-resistant degree of hardness were further excellent is desired.

[0005] Then, [** JP,62-56565,A, **J.Vac.Sci.Technol.A4 (6) as which the coats by the ion-plating method or the sputtering method (TiAl), such as N, C (TiAl), and CN (TiAl), were proposed as a coat which can respond to these requests, 1986, p 2717, and **J.Vac.Sci.Technol.A4 (6), 1986, p 2695, and **J.of Solid -- state -- Chemistry -- 70 -- 1987 -- a year -- P -- 318 --] -- ** -- Surface -- Engineering -- Conf. -- ' -- 85 -- Vol. -- III : 197 or paper 44 and p 1985, and ** German JP,3611492,B A1 --] . Moreover, **Thin Solid Films, 153 (1987), and p67-74] were proposed as a method using cathode arc electric discharge.

[0006]

[Problem(s) to be Solved by the Invention] However, there were the following problems in formation of a coat such conventionally.

** it is described as C (TiAl), N (TiAl), and (TiAl) CN by JP,62-56565,A -- *** -- it stops, and if the proportion of Ti and aluminum and the proportion of C and N are adjusted how, there is no clear description about the point what effect arises

**J. Vac.Sci.Technol. and A4 In N (Ti, aluminum), two things of composition of Ti:aluminum=75:25 and Ti:aluminum=50:50 are described by p 2717 in (6) year [1986].

**J. Vac.Sci.Technol.A4 p 2695 will have the indication about N (Ti, aluminum) in (6) year [1986], and the maximum content of aluminum is Ti:aluminum=45:55 also in here.

[0007] ** J.of Solid State Chemistry 70 and 1987 a year and P 318 (1987) -- N (Ti, aluminum) -- setting -- under [all] composition -- aluminum -- 30at% -- it is described that it can dissolve However, since the content of Ti is not measured here, the inclusion proportion of Ti and aluminum, i.e., the mole ratio of Ti and aluminum, cannot be specified.

** Surface Engineering Conf.'85, Vol.III : Although there will be an indication about N (Ti, aluminum) also in 197 or paper 44 and p 1985, this is the same as that of ** in content according to the same author as the aforementioned **.

** German JP,3611492,B A1 it attaches and states to target composition -- *** -- it stops and reference is not made about coat composition and the relation of the operation effect

** Thin Solid Films, 153 (1987), and p67-74] are attached to the whole coat composition, and nothing describes them, and they are not ****ing about coat composition and especially the relation of the operation effect, either.

[0008] In few composition of aluminum content indicated by the above-mentioned ** - **, the high temperature conductivity or oxidation resistance of AlN cannot say that it can demonstrate enough so that it can understand from a publication of the after-mentioned example about this invention.

[0009] Then, this invention tends to be investigated in detail about an AlN-TiN system all composition region, AlN tends to be considered as basic composition, the weak point of AlN independent composition tends to be improved by dissolution of TiN, the composition region tends to be pinpointed, and it is going to offer the wear-resistant member by which adhesion was improved [covering formation] the coat excellent in abrasion resistance, oxidation resistance, and the degree of hardness.

[0010]

[Means for Solving the Problem] this invention is the following chemical composition (Al_xTi_{1-x})(N_yC_{1-y}) to a base-material front face.

however -- It is the wear-resistant member with which it comes to cover the wear-resistant coat of 0.8 to 10

micrometer thickness shown by $0.56 \leq x \leq 0.75$, $0.6 \leq y \leq 1$.

[0011]

[Embodiments of the Invention] In forming the wear-resistant coat of this invention, a metal component is ionized by the arc discharge which makes a cathode an evaporation source, and it carries out by the PVD represented at the ion-plating method, the sputtering method, etc., for example. Among these, when the case where it carries out, for example by the ion-plating method is taken up typically and explained, it is the metal component ionized as mentioned above N₂ The ambient atmosphere, or N₂ / CH₄ It is made to react in the ambient atmosphere. It is Al_x Ti_{1-x} which consists of the purpose composition itself although Ti and aluminum can also be individually used as a cathode, respectively. A target, then control of coat composition are easy. Since vaporization of each alloy content in this case is performed in a high current region A [some dozens of] or more, a composition gap of the cathode matter does not have *****. And an ionization efficiency is highly rich in reactivity, and the coat which was excellent in adhesion is obtained by impressing bias voltage to a substrate.

[0012] Thus, composition of the coat obtained (Al_x Ti_{1-x}) (N_y C_{1-y})

however — It is required to be $0.56 \leq x \leq 0.75$, $0.6 \leq y \leq 1$, and it is $0.60 \leq x \leq 0.70$ preferably.

[0013] When the nitride system explained on behalf of this, the solid solution of this invention which consists of the above-mentioned coat composition was solid solution which considers AlN-TiN as edge composition, and as a result of investigating about various component domains, it became clear [having the crystal structure which is shown in the drawing 1 and the drawing 2]. drawing 1 — setting — (P) NaCl type (B1 structure) field and (Q) It is ZnS type (Ur. Die Zeit type) field. namely, composition within the limits which as for the component domain of this invention has B1 structure so that clearly from drawings 1 and 2 — it is — AlN — TiN — 25-44 mol % — it is the solid solution which dissolved The ground limited to this domain is described below.

[0014] As a result of coat composition resembling AlN when the amount (x) of aluminum exceeds 0.75 so that clearly from drawing 2 , cause elasticity-ization of a coat, it stops obtaining sufficient degree of hardness, and a flank wear is caused easily. On the other hand, if x becomes 0.75 or less, a coat will be formed into a high degree of hardness, and flank abrasion loss will decrease. Furthermore, drawing 3 is a graph which shows the relation between x and a degree of hardness in N (Al_x Ti_{1-x}), and when x exceeds 0.75, it understands that a degree of hardness falls greatly. The upper limit of x was determined as 0.75 from these.

[0015] However, in order to demonstrate the high-temperature-oxidation-proof property of AlN effectively, it turns out that there is a lower limit which is described below. namely, (Al_x Ti_{1-x}), N[however x= 0, and 0. — when change of the oxidation increase in quantity to the temperature change at the time of carrying out temperature-up oxidation of 25, 0.5, and 0.6] by part for 5 degrees-C/of programming rates among the atmospheric air was measured, the result shown in drawing 4 was obtained Drawing 4 shows that oxidation start temperature rises as the amount of aluminum increases. On the other hand, in order to fully suppress oxidation of the coat by elevation of the edge-of-a-blade temperature under tool cutting, it is necessary to reduce the amount of craters by cutting heat. When drawing 4 is seen from such a viewpoint, it turns out that it is effective to consider as the composition domain which was rich in AlN component as much as possible. Drawing 5 is the graph packed in relation with the value of x, and oxidation start temperature in N (Al_x Ti_{1-x}). In consideration of synthesizing the result shown in these graphs, and becoming 800 degrees C or more, while tool edge-of-a-blade temperature cuts, oxidation start temperature decided composition of 800 degrees C or more to be $x = 0.56$.

[0016] Moreover, in this invention, the high degree-of-hardness nature (ordinary temperature degree-of-hardness Hv: about 3100kg/mm²) of TiC is exhibited by forming a charcoal nitride. That is, in the empirical formula of this invention, the degree of hardness of abrasion resistance [a large next door and] improves as the value of y decreases. Drawing 6 covers [(N_y (aluminum_{0.65}Ti_{0.35}) C_{1-y}) y= 0.4, 0.6, 0.8, 0.9, and 1] for a superhard chip (let WC-10% Co be a principal component). [however,] [3-micrometer] The result which measured the amount of craters of 15 minutes after when cutting **ed material S50C by the cutting speed of 170m / min, the feed rate of 0.25mm / rev, and 0.1mm of slittings is shown. y is 0.6 so that it may see at this result. If it becomes the following, oxidation resistance will fall and it will become easy to cause a crater. $y \geq 0.6$ An oxidation-resistant remarkable fall is not seen in the domain.

[0017] In addition, a thickness is 0.8 so that clearly from the example and the example of a comparison which are mentioned later. If abrasion resistance becomes inadequate and 10 micrometers is exceeded on the other hand when it is under mum, a crack will become easy to go into the layer itself, and an intensity will become inadequate. it is as being naturally understood from the above-mentioned explanation that it is not what is boiled and restricted especially in base-material composition, a base-material configuration, intended use, etc. as a wear-resistant covering member of this invention

[0018] Although an example is explained below, this invention not being limited to the following example, marking a front and the after-mentioned meaning, and carrying out a design change suitably is included in the technical domain of this invention.

[0019]

[Example]

(A) As an example of a cutting tool, the chip was chosen and the following samples were produced.

Example 1aluminum_{0.6} Ti_{0.4} The chip made from a cemented carbide (principal component:WC-10% Co) was attached in the substrate electrode holder of the cathode arc method ion plating system used as a cathode electrode. The heaters for securing the homogeneity of the wear-resistant coat formation status, such as a base-material rolling mechanism, were installed in **** equipment.

[0020] While the bias voltage of -70V is impressed to a base material, carrying out the heating hold of the base-material temperature at a heater in membrane formation at 400 degrees C, it is a high grade N₂ in equipment. Gas is introduced to 7x10⁻³Torr, arc discharge is started, and it is 4 micrometers of thicknesss to a base-material front face. The coat was formed. Measurement of a thickness fractures one in the base material simultaneously attached in the substrate electrode holder, and observes and measures a layer cross section by the scanning electron microscope. Furthermore, the determination of layer composition analyzed the layer depth orientation by the Auger-analysis method per [which was similarly attached simultaneously] base material. As a result, there was no concentration change in the layer thickness orientation of aluminum, Ti, and N, it was fixed and the peak height of each component element to layer composition was N (aluminum_{0.62}Ti_{0.38}). The metal component ratios Ti/aluminum in a layer do not have a cathode component ratio and a gap, and can be called ***** identity.

[0021] Example 2aluminum_{0.7} Ti_{0.3} Except having used the cathode, membranes were formed on the same conditions as an example 1. The thickness which formed membranes is 3.8. It was mum and was layer composition

(aluminum0.67Ti0.33) N.

They are N₂ / CH₄ as example 3 reactivity gas. Membranes were formed on the same conditions as an example 1 except having used mixed gas. The thickness which formed membranes is 4.3. It was mum and was layer composition (N(aluminum0.61Ti0.39)0.7 C0.3).

[0022] The following chip sample was created for the comparison.

The example of sample comparison 2Ti cathode which does not form a coat in the base material of example of comparison 1 example 1 is used, and it is N₂. Gas was introduced to 7x10⁻³Torr, and TiN was formed on the same conditions as an example 1. The thickness which formed membranes is 4.3. It was mum.

[0023] Same aluminum0.6 Ti0.4 as the cathode matter used for the crucible in the example 1 as a source of heating of example of comparison 3 evaporator using the ion plating system which used the electron beam The solid solution was inserted in and the chip made from a cemented carbide was attached in the substrate electrode holder. The heater was installed, while the substrate rolling mechanism etc. was installed, in order to secure membranous homogeneity and membranous adhesion. having carried out the heating hold of the base-material temperature at the heater in membrane formation at 400 degrees C -- a base material -- the bias voltage of -600V -- impressing -- the inside of equipment -- high grade N₂ 7x10⁻⁴ Torr up to -- it introduced and membranes were formed to the base material by the ion-plating method The thickness could be 4 micrometers. As a result of analyzing a coat by the still same analytical method as an example 1, the ratio of concentration of aluminum and Ti was uneven in the orientation of a thickness, and the membranous component ratio has not been specified. Especially, concentration of aluminum is observed by the interface of a base material and a layer, and it is thought that aluminum carried out vaporization adhesion preferentially in early stages of electron beam melting.

[0024] Furthermore, the following comparison chip sample was made. Each layer composition and thickness are shown.

Example of example of example of comparison 4 layer composition:(aluminum0.78Ti0.22) N thickness:3micrometer

comparison 5 layer composition:(aluminum0.42Ti0.58) N thickness:4micrometer comparison 6 layer

composition:(aluminum0.64Ti0.36) N thickness:0.7 Example of mum comparison 7 layer

composition:(aluminum0.64Ti0.36) N thickness:12micrometer[0025] The following cutting conditions performed the cutting examination for 10 minutes using the chip sample obtained by the examples 1-3 and the examples 1-7 of a comparison. Frank abrasion loss and a crater depth are shown in Table 1.

Cutting-conditions: **-ed material S50C cutting speed 170m / min feed rate It cuts deeply 0.25 mm/rev. 0.1 mm

[0026]

[Table 1]

	フランク摩耗量 (mm)	クレータ摩耗深さ (μm)
実施例 1	0.37	5
〃 2	0.38	4
〃 3	0.36	7
比較例 1	0.48	43
〃 2	0.15	18
〃 3	0.21	25
〃 4	途中で膜剥離 (中断)	—
〃 5	0.09	10
〃 6	欠損	—
〃 7	欠損	—

[0027] The example of this invention showed the abrasion resistance which was excellent in each compared with the example of a comparison so that more clearly than Table 1.

[0028] (B) As an example of a cutting tool, the drill was chosen and the following samples were produced.

Membrane formation was formed in the carbide drill (let WC-8% Co be a principal component) of 46mm [of examples] phi on the same conditions as an example 1. The layer composition at this time is N (aluminum0.65Ti0.35), and a thickness is 4.5. It was mum.

[0029] The following drill sample was prepared as an example of a comparison.

Membrane formation was formed in the carbide drill of 86mm [of the examples of a comparison] phi on the same conditions as the example 5 of a comparison. The layer composition at this time was N (aluminum0.46Ti0.54), and the thickness was 4 micrometers. Furthermore, the following comparison drill sample was manufactured. Each layer composition and thickness are shown.

[0030] Example of example of example of comparison 9 layer composition:TiN thickness:5micrometer comparison 10

layer composition:(aluminum0.64Ti0.36) N thickness:0.7micrometer comparison 11 layer

composition:(aluminum0.64Ti0.36) N thickness:12micrometer[0031] The following cutting conditions performed hole down using the drill sample obtained by the example 4 and the examples 8-10 of a comparison. It is shown in Table 2, using a result as the hole down number.

Cutting-conditions: **-ed material S50C, 13mm cutting speed 50m / min feed rate 0.2 mm/rev lubrication [0032] by the emulsion

[Table 2]

	穴用寸個数	摩耗状況
実施例 4	7100	正常摩耗
比較例 8	3500	膜剥離
比較例 9	2100	欠損発生
比較例 10	810	欠損発生
比較例 11	2000	膜剥離

[0033] Compared with the example of a comparison, the steep increase in the hole down number accepted, and the tool obtained by this invention technique so that more clearly than Table 2 had good abrasion resistance.

[0034] (C) As an example of a cutting tool, the high-speed-steel drill was chosen and the following samples were produced.

Membrane formation was formed in 56mm phi high-speed-steel drill of examples on the same conditions as an example 1. It is N (aluminum0.63Ti0.37) and layer composition is a thickness 5.5 It was referred to as mum. The following high-speed-steel drill sample was prepared as an example of a comparison.

TiN was formed on the same conditions as the example 2 of a comparison on 126mm phi high-speed-steel drill of the examples of a comparison. The thickness was 5 micrometers.

[0035] Furthermore, the following comparison high-speed-steel drill sample was manufactured. Each layer composition and thickness are shown.

Example of comparison 13 layer composition:(aluminum0.43Ti0.57) N thickness:4.5 The following cutting conditions performed hole down using the high-speed-steel drill sample obtained by the example of mum comparison 14 layer composition:(aluminum0.63Ti0.37) N thickness:13micrometer example 5, and the examples 12-14 of a comparison. It is shown in Table 3, using a result as the hole down number.

[0036]

[Table 3]

	穴用寸個数	摩耗状況
実施例 5	2500	正常摩耗
比較例 12	600	正常摩耗
比較例 13	1300	欠損発生
比較例 14	850	欠損発生

[0037] Cutting-conditions: **ed material S50C, 10mm cutting speed 30m / min feed rate 0.15mm / rev lubrication Compared with the example of a comparison, the steep increase in the hole down number was seen, and the high-speed-steel drill obtained by this invention technique so that more clearly than Table 3 by the emulsion had good abrasion resistance.

[0038]

[Effect of the Invention] Since it is constituted as mentioned above, it differs from the conventional N (Ti, aluminum) based on TiN, and this invention is IIIb. Since it was the coat to which Ti dissolved to AlN which is a group's nitride, the outstanding property approximated to AlN is demonstrated about thermal resistance, thermal conductivity, etc., and it succeeded in offering the wear-resistant member by which adhesion was improved [covering formation] the coat which was excellent in abrasion resistance, oxidation resistance, and the degree of hardness as the result.

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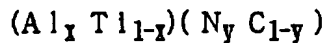
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(56)参考文献 特開 昭64-11961 (J P, A)
日本金属学会誌, 57〔8〕(1993) 池田、佐藤、P. 919-925

(54)【発明の名称】 耐摩耗性皮膜被覆部材

(57)【特許請求の範囲】

【請求項1】 基材表面に、



但し $0.56 \leq x \leq 0.75$

$0.6 \leq y \leq 1$

で示される化学組成からなり、且つNaCl型の結晶構造を有する厚さ0.8-10μmの耐高温酸化性に優れた高硬度耐摩耗性皮膜が形成されたものであることを特徴とする耐摩耗性皮膜被覆部材。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、フライス加工工具等で代表される様な耐摩耗性の要求される部材に関し、詳細には基材表面に、耐摩耗性、耐熱性、硬度などの優れた

耐摩耗性皮膜が優れた密着性をもって被覆形成されてなる耐摩耗性皮膜被覆部材に関するものである。

【0002】

【従来の技術】高速度工具鋼や超硬合金工具鋼等を製作する場合は、耐摩耗性等の性能をより優れたものとするを目的として、工具基材の表面にTi等の窒化物や炭化物よりなる耐摩耗性皮膜を形成することが行なわれている。このような要求がなされる工具としては、チップ、バイト、カッター、エンドミル、ドリルなどの切削工具；チップ、金型、ダイス、ロール、剪断工具などの耐摩耐蝕工具；或はビット、ロッドなどの鉋山土木工具が知られている。

【0003】基材表面に耐摩耗性皮膜を形成する方法としては、従来よりCVD法（化学的蒸着法）及びPVD法（物理的蒸着法）が知られている。しかし前者の方法

では高温処理に起因して母材の特性が劣化する恐れがあるので、工具等の耐摩耗性皮膜としては、後者の方法で形成したTiN等の皮膜等が汎用されていた。TiN皮膜は耐熱性が良好であって、切削時の加工熱や摩擦熱による工具すくい面のクレータ摩耗を抑制する機能を発揮する。

【0004】しかしながら近年、例えば切削工具の分野では、切削速度の一層の高速化が要望されており、切削条件の過酷化が進行しつつある為、上記した様な従来の耐摩耗性皮膜ではこの要請に十分に答えられないものとなった。或は切削工具以外の工具分野、例えば耐摩耐蝕工具、鉱山土木工具など、さらには工具以外の各種機械分野においても使用条件の過酷化が進んでおり、耐摩耗性の一層の向上と耐熱性や硬度が更に優れた皮膜の開発が望まれている。

【0005】そこでこれらの要請に応え得る皮膜として、イオンプレーティング法やスパッタリング法による(TiAl)N、(TiAl)C、(TiAl)CN等の皮膜が提案された[①特開昭62-56565, ②J. Vac. Sci. Technol. A4 (6), 1986年, p 2717, ③J. Vac. Sci. Technol. A4 (6), 1986年, p 2695, ④J. of Solid state Chemistry 70, 1987年, P 318], ⑤Surface Engineering Conf. '85, Vol. III : paper 44, p197, 1985年, ⑥ドイツ特許3611492A1]。またカソードアーク放電を利用した方式として⑦Thin Solid Films, 153(1987), p67-74が提案された。

【0006】

【発明が解決しようとする課題】しかしながらこの様な従来皮膜の形成には、次の様な問題があった。

①特開昭62-56565には、(TiAl)C、(TiAl)Nおよび(TiAl)CNと記述されているに止まり、TiとAlの比率、またCとNの比率をどのように調整すればどのような効果が生じるかといった点については明確な記述がない。

②J. Vac. Sci. Technol. A4 (6), 1986年, p 2717には(Ti, Al)NにおいてTi:Al=75:25, Ti:Al=50:50の組成のものが2例記述されている。これらの組成を固溶体成分で記述すれば、TiN-A1N固溶体と表現できるが、TiNを基本組成としてA1Nが最高50モル%固溶したものと言える。

③J. Vac. Sci. Technol. A4 (6), 1986年, p 2695にも(Ti, Al)Nについての開示があるが、ここにおいてもAlの最大含有量はTi:Al=45:55である。

【0007】④J. of Solid State Chemistry 70, 1987年, P 318 (1987年)には、(Ti, Al)Nにおいて、全組成中にAlが30at%固溶できると記述されている。

⑤Surface Engineering Conf. '85, Vol. III : paper 44, p197, 1985年にも(Ti, Al)Nについての開示があ

るが、これは前記③と同一の著者によるものであり、内容的には③と同一である。

⑥ドイツ特許3611492A1はターゲット組成に付いて述べているに止まり、皮膜組成と作用効果の関係については言及されていない。

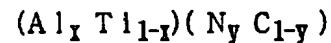
⑦Thin Solid Films, 153(1987), p67-74は皮膜組成全体に付いて何も述べておらず、また皮膜組成と作用効果の関係についても特には言及していない。

【0008】上記①～③で開示されたA1含有量の少ない組成では、本発明に関する後記実施例の記載から理解できる様に、A1Nの高熱伝導性や耐酸化性が十分発揮できるとは言えないものである。

【0009】そこで本発明は、A1N-TiN系全組成域について詳細に調べ、A1Nを基本組成としてA1N単独組成の弱点をTiNの固溶により改善し、その組成域を特定したものであって、耐摩耗性、耐酸化性及び硬度に優れた皮膜が密着性良く被覆形成された耐摩耗性部材を提供しようとするものである。

【0010】

【課題を解決するための手段】本発明は基材表面に、下記化学組成



$$\text{但し } 0.56 \leq x \leq 0.75$$

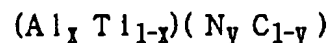
$$0.6 \leq y \leq 1$$

で示され、且つNaCl型の結晶構造を有する厚さ0.8-10μmの耐高温酸化性に優れた高硬度耐摩耗性皮膜が被覆されてなる耐摩耗性部材である。

【0011】

【作用】本発明の耐摩耗性皮膜を形成するに当たっては、例えば、カソードを蒸発源とするアーク放電によって金属成分をイオン化するものであって、イオンプレーティング法やスパッタリング法等に代表されるPVD法によって行なう。これらのうち例えばイオンプレーティング法で行なう場合を代表的に取り上げて説明すると、前記の様にイオン化した金属成分を、N₂雰囲気又はN₂/CH₄雰囲気中で反応させる。カソードとしてはTi及びAlをそれぞれ個別に使用することもできるが、目的組成そのものからなるAl_xTi_{1-x}をターゲットとすれば、皮膜組成のコントロールが容易である。この場合の各合金成分の蒸発は、数十アンペア以上の大電流域で行なわれるため、カソード物質の組成ずれは殆んど生じない。しかもイオン化効率が高く反応性に富み、基板にバイアス電圧を印加することによって密着性の優れた皮膜が得られる。

【0012】この様にして得られる皮膜の組成は



$$\text{但し } 0.56 \leq x \leq 0.75$$

$$0.6 \leq y \leq 1$$

であることが必要であり、且つNaCl型の結晶構造を有するものである。そしてその厚さは、 $0.8-10\mu\text{m}$ であり、これらの要件を満足することによって、耐高温酸化性に優れた高硬度耐摩耗性皮膜としての特性を発揮する。尚上記xのより好ましい範囲は $0.60 \leq x \leq 0.70$ である。

【0013】上記皮膜組成からなる本発明の固溶体は、これを窒化物系で代表して説明すると、AlN-TiNを端組成とする固溶体であり、種々の成分範囲について調べた結果、図1及び図2に示すような結晶構造を有することが明らかとなった。図1において、(P)はNaCl型(B1構造)領域、(Q)はZnS型(ウルツァイト型)領域である。即ち本発明の成分範囲は、図1、2から明らかな様に、NaCl型(B1構造)を有する組成範囲内で、AlNにTiNが25~44モル%固溶した固溶体である。この範囲に限定した理由を以下に述べる。

【0014】図2から明らかな様に、Al量(x)が0.75を超える場合は、皮膜組成がAlNに近似してくる結果、皮膜の軟質化を招き、十分な硬度が得られなくなり、フランク摩耗を容易に引き起す。一方xが0.75以下になると、皮膜は高硬化化し、フランク摩耗量は減少する。更に図3は、 $(Al_x Ti_{1-x})N$ におけるxと硬度の関係を示すグラフであり、xが0.75を超えると硬度が大きく低下することが分かる。これらからxの上限を0.75と定めた。但しより好ましい上限は前述の如く0.70である。

【0015】しかしAlNの耐高温酸化特性を有効に発揮するためには次に述べる様な下限があることが分かった。即ち $(Al_x Ti_{1-x})N$ [但し $x=0, 0.25, 0.5, 0.6$]を、大気中、昇温速度 $5^\circ\text{C}/\text{分}$ で昇温酸化した場合の温度変化に対する酸化増量の変化を測定したところ、図4に示す結果が得られた。図4より、Al量が増加するにつれて酸化開始温度が上昇することがわかる。一方工具切削中の刃先温度の上昇による皮膜の酸化を十分に抑制する為には、切削熱によるクレータ摩耗量を低下させる必要がある。この様な観点から図4を見ると、できる限りAlN成分に富んだ組成範囲とすることが有効であることがわかる。図5は $(Al_x Ti_{1-x})N$ におけるxの値と酸化開始温度の関係でまとめたグラフである。これらのグラフで示される結果を総合し、且つ工具刃先温度が切削中に 800°C 以上になることを考慮して、酸化開始温度が 800°C 以上の組成を $x=0.56$ と決めた。

【0016】また本発明では、炭窒化物を形成することによってTiCの高硬度性(常温硬度Hv:約 $3100\text{kg}/\text{mm}^2$)を発揮させるものである。即ち本発明の組成式においては、yの値が減少するにつれて硬度が大となり、耐摩耗性は向上する。図6は、超硬チップ(WC-10%Coを主成分とする)に、 $(Al_{0.65} Ti_{0.35})$

$(Ny C_{1-y})$ [但し $y=0.4, 0.6, 0.8, 0.9, 1$]を $3\mu\text{m}$ 被覆し、被削材S50Cを切削速度 $170\text{m}/\text{min}$ 、送り速度 $0.25\text{mm}/\text{rev}$ 、切り込み 0.1mm で切削した時の15分後のクレータ摩耗量を測定した結果を示す。この結果にみられるように、yが0.6未満になると耐酸化性が低下してクレータ摩耗を起し易くなる。y ≥ 0.6 の範囲では耐酸化性の顕著な低下はみられない。

【0017】尚後述する実施例及び比較例から明らかな様に、膜厚が $0.8\mu\text{m}$ 未満の場合は耐摩耗性が不十分となり、一方 $10\mu\text{m}$ を超えると膜自体にクラックが入り易くなって強度が不十分となる。本発明の耐摩耗性被覆部材としては、基材組成、基材形状、用途等において特に制限されるものでないことは上記説明から自ずと理解される通りである。

【0018】以下実施例について説明するが、本発明は下記の実施例に限定されるものではなく、前・後記の趣旨に倣して適宜設計変更することは本発明の技術的範囲に含まれる。

【0019】

【実施例】(A)切削工具の一例としてチップを選び、以下の試料を作製した。

実施例1

$Al_{0.6} Ti_{0.4}$ をカソード電極とするカソードアーク方式イオンプレーティング装置の基板ホルダーに、超硬合金製チップ(主成分:WC-10%Co)を取付けた。尚本装置には、耐摩耗性皮膜形成状態の均一性を確保する為の基材回転機構等及びヒータを設置した。

【0020】成膜に当たっては、ヒータによって基材温度を 400°C に加熱保持したまま、基材に -70V のバイアス電圧を印加すると共に、装置内に高純度 N_2 ガスを $7 \times 10^{-3}\text{Torr}$ まで導入し、アーク放電を開始して基材表面に膜厚 $4\mu\text{m}$ の皮膜を形成した。膜厚の測定は、基板ホルダーに同時に取り付けた基材の内の1個を破断し、膜断面を走査型電子顕微鏡で観察して測定したものである。さらに膜組成の定量は、同じく同時に取り付けた基材につきオージェ分光分析法により膜深さ方向の分析を行なった。その結果Al, Ti, Nの膜厚さ方向には濃度変化がなく一定で、各成分元素のピーク高さから、膜組成は $(Al_{0.62} Ti_{0.38})N$ であった。膜中の金属成分比Ti/Alはカソード成分比とずれがなく殆んど同一といえる。

【0021】実施例2

$Al_{0.7} Ti_{0.3}$ カソードを用いた以外は、実施例1と同一条件で成膜を行なった。成膜した膜厚は $3.8\mu\text{m}$ であり、膜組成は $(Al_{0.67} Ti_{0.33})N$ であった。

【0022】実施例3

反応性ガスとして N_2/CH_4 混合ガスを用いた以外は実施例1と同一条件で成膜を行なった。成膜した膜厚は $4.3\mu\text{m}$ であり、膜組成は $(Al_{0.61} Ti_{0.39})N$

0.7 C_{0.3})であった。比較のために下記チップ試料を作成した。

【0023】比較例1

実施例1の基材に皮膜を形成しない試料

比較例2

Tiカソードを用いてN₂ ガスを7×10⁻³ Torrまで導入し実施例1と同一条件でTiNの成膜を行なった。成膜した膜厚は4.3 μmであった。

【0024】比較例3

蒸発器の加熱源として電子ビームを使用したイオンブレーティング装置を用いて、るつばに実施例1で使用したカソード物質と同一のAl_{0.6} Ti_{0.4} 固溶体を装入し、基板ホルダーには超硬合金製チップを取り付けた。膜の均一性及び膜の密着性を確保するため、基板回転機構等を設置すると共に、ヒーターを設置した。成膜にあたってはヒーターにより基材温度を400℃に加熱保持したまま、基材に-600Vのバイアス電圧を印加し、装置内に高純度N₂ を7×10⁻⁴ Torrまで導入しイオンブレーティング法により基材に成膜を行なった。膜厚は4 μmとした。さらに実施例1と同様の分析方法により皮膜を分析した結果、AlとTiの濃度比が膜厚方向に不均一で膜の成分比は規定できなかった。特に基材と膜の界面にはAlの濃縮が観察され、電子ビーム溶解の初期にAlが優先的に蒸発付着したものと考えられる。更に下記の比較チップ試料を制作した。夫々の膜組成と

膜厚を示す。

【0025】

比較例4

膜組成：(Al_{0.78} Ti_{0.22}) N

膜厚：3 μm

比較例5

膜組成：(Al_{0.42} Ti_{0.58}) N

膜厚：4 μm

比較例6

膜組成：(Al_{0.64} Ti_{0.36}) N

膜厚：0.7 μm

比較例7

膜組成：(Al_{0.64} Ti_{0.36}) N

膜厚：12 μm

【0026】実施例1～3及び比較例1～7によって得られたチップ試料を用い、下記切削条件により10分間の切削試験を行った。フランク摩耗量及びクレータ摩耗深さを表1に示す。

切削条件：

被削材 S50C

切削速度 170 m/min

送り速度 0.25 mm/rev

切り込み 0.1 mm

【0027】

【表1】

	フランク摩耗量 (mm)	クレータ摩耗深さ (μm)
実施例 1	0.07	5
〃 2	0.08	4
〃 3	0.06	7
比較例 1	0.48	43
〃 2	0.15	18
〃 3	0.21	25
〃 4	5分で膜剥離(中断)	—
〃 5	0.09	10
〃 6	欠損	—
〃 7	欠損	—

【0028】表1より明らかな様に、本発明の実施例は、いずれも比較例に比べて優れた耐摩耗性を示した。

(B) 切削工具の一例としてドリルを選び、以下の試料を作製した。

【0029】実施例4

6mmφの(WC-8%Coを主成分とする)超硬ドリルに実施例1と同一条件にて成膜を形成した。このときの膜組成は(Al_{0.65} Ti_{0.35}) Nであり、膜厚は4.5 μmであった。比較例として次のドリル試料を用意した。

【0030】比較例8

6mmφの超硬ドリルに比較例5と同一条件にて成膜を形成した。このときの膜組成は(Al_{0.46} Ti_{0.54})Nであり、膜厚は4μmであった。更に下記の比較ドリル試料を製作した。夫々の膜組成と膜厚を示す。

【0031】

比較例9

膜組成：TiN

膜厚：5μm

比較例10

膜組成：(Al_{0.64} Ti_{0.36})N

膜厚：0.7μm

比較例11

膜組成：(Al_{0.64} Ti_{0.36})N

膜厚：12μm

【0032】実施例4及び比較例8～10によって得られたドリル試料を用い、下記切削条件により穴明けを行った。結果を穴明け個数として表2に示す。

切削条件：

被削材 S50C、13mm^φ

切削速度 50m/min

送り速度 0.2mm/rev

潤滑 エマルジョンによる

【0033】

【表2】

	穴明け個数	摩耗状況
実施例4	7100	正常摩耗
比較例8	3500	膜剥離
比較例9	2100	欠損発生
比較例10	810	欠損発生
比較例11	2000	膜剥離

【0034】表2より明らかな様に本発明方法で得られた工具は、比較例に比べて穴明け個数の大幅な増加が認められ、耐摩耗性が良好であった。(C)切削工具の一例としてハイスドリルを選び、以下の試料を作製した。

【0035】実施例5

6mmφハイスドリルに実施例1と同一条件にて成膜を形成した。膜組成は(Al_{0.63} Ti_{0.37})Nであり、膜厚を5.5μmとした。比較例として次のハイスドリル試料を用意した。

【0036】比較例12

6mmφハイスドリルに比較例2と同一条件でTiNを成膜した。膜厚は5μmであった。更に下記の比較ハイス

ドリル試料を製作した。夫々の膜組成と膜厚を示す。

【0037】比較例13

膜組成：(Al_{0.43} Ti_{0.57})N

膜厚：4.5μm

比較例14

膜組成：(Al_{0.63} Ti_{0.37})N

膜厚：13μm

実施例5及び比較例12～14によって得られたハイスドリル試料を用い、下記切削条件により穴明けを行った。結果を穴明け個数として表3に示す。

【0038】

【表3】

	穴明け個数	摩耗状況
実施例 5	2500	正常摩耗
比較例 1 2	600	正常摩耗
比較例 1 3	1300	欠損発生
比較例 1 4	850	欠損発生

【0039】

切削条件：

被削材 S50C, 10mm^φ

切削速度 30m/min

送り速度 0.15mm/rev

潤滑 エマルジョンによる

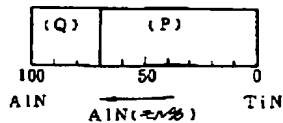
表3より明らかな様に本発明方法で得られたハイスドリルは、比較例に比べて穴明け個数の大幅な増加がみられ、耐摩耗性が良好であった。

【0040】

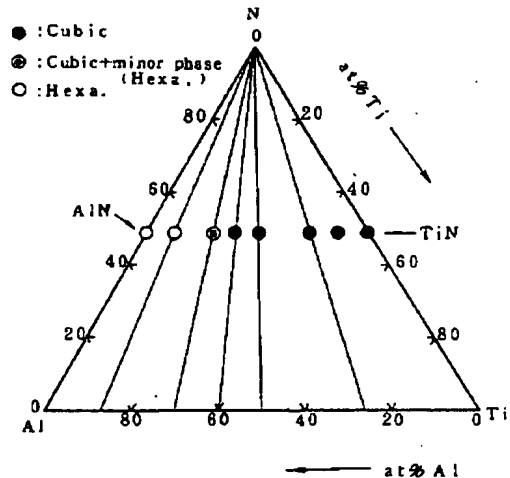
【発明の効果】本発明は以上の様に構成されているので、TiNを基本とした従来の(Ti, Al)Nと異なり、III_b族の窒化物であるAlNにTiが固溶した皮膜である為、耐熱性、熱伝導性等に関し、AlNに近似した優れた特性が発揮され、その結果として、耐摩耗性、耐高温酸化性及び硬度に優れた皮膜が密着性良く被覆形成された耐摩耗性皮膜被覆部材を提供することに成功した。

【図面の簡単な説明】

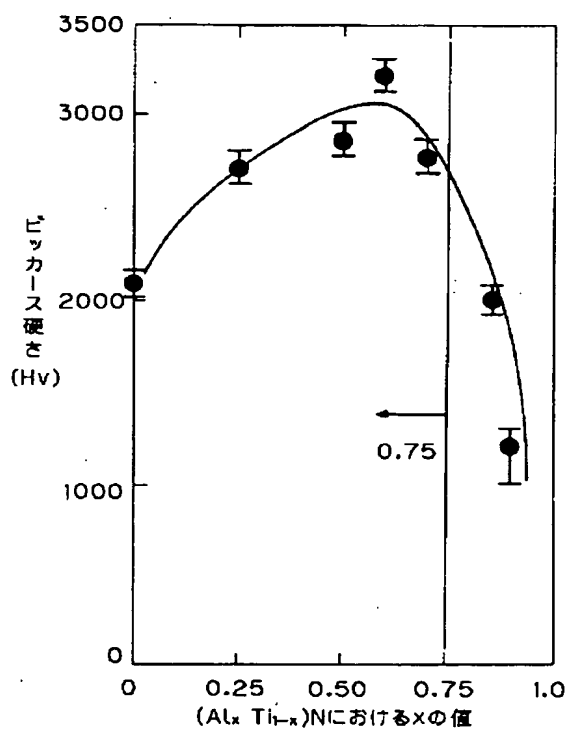
【図1】



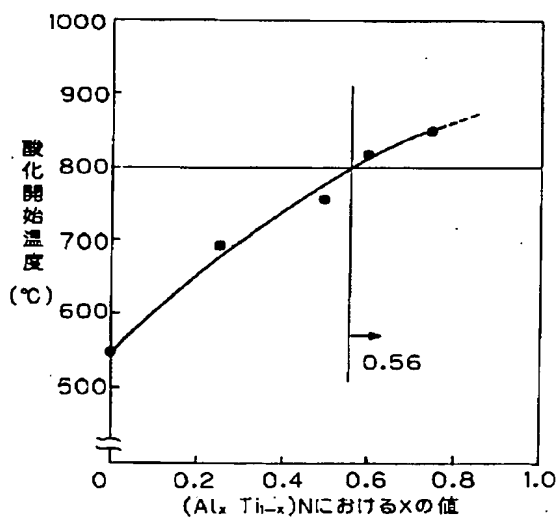
【図2】



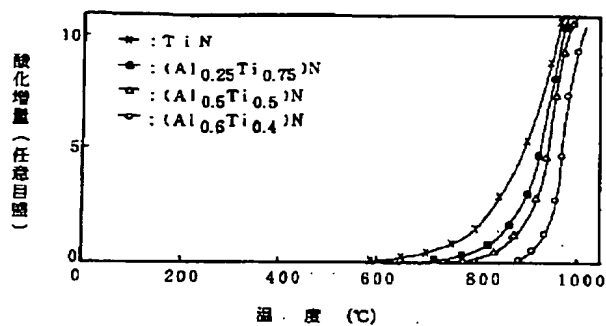
【図3】



【図5】



【図4】



【図6】

